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High accuracy calculations of the rotation-vibration spectrum of H_3^+

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Abstract. Calculation of the rotation-vibration spectrum of H_3^+ , as well as of its deuterated isotopologues, with near-spectroscopic accuracy requires the development of sophisticated theoretical models, methods, and codes. The present paper reviews the state-of-the-art in these fields. Computation of rovibrational states on a given potential energy surface (PES) has now become standard for triatomic molecules, at least up to intermediate energies, due to developments achieved by the present authors and others. However, highly accurate Born–Oppenheimer (BO) energies leading to highly accurate PESs are not accessible even for this two-electron system using conventional electronic structure procedures (*e.g.*, configuration-interaction or coupled-cluster techniques with extrapolation to the complete (atom-centred Gaussian) basis set limit). For this purpose highly specialized techniques must be used, *e.g.*, those employing explicitly correlated Gaussians and nonlinear parameter optimizations. It has also become evident that a very dense grid of *ab initio* points is required to obtain reliable representations of the computed points extending from the minimum to the asymptotic limits. Furthermore, adiabatic, relativistic, and quantum electrodynamics (QED) correction terms need to be considered to achieve near-spectroscopic accuracy during calculation of the rotation-vibration spectrum of H_3^+ . The remaining and most intractable problem is then the treatment of the effects of non-adiabatic coupling on the rovibrational energies, which, in the worst cases, may lead to corrections on the order of several cm^{-1} . A promising way of handling this difficulty is the further development of effective, motion- or even coordinate-dependent, masses and mass surfaces. Finally, the unresolved challenge of how to describe and elucidate the experimental pre-dissociation spectra of H_3^+ and its isotopologues is discussed.

1. Introduction

The highly stable molecular ion H_3^+ , the prototype of a three-centre two-electron (3c-2e) chemical bond, is rapidly formed in an exoergic (exergonic) reaction following the collision of molecular hydrogen and its cation,

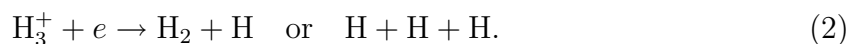


The high stability of the ion means that H_3^+ is the dominant molecular ion in cold hydrogen plasmas, which of course make up much of the known Universe. H_3^+ has long been thought to be the initiator of much of gas-phase interstellar chemistry via the ion-molecule reactions $H_3^+ + X \rightarrow HX^+ + H_2$ (where X can be an atom or a molecule) (Watson 1973, Herbst & Klemperer 1973, Oka 2013, Millar 2015), but its rather limited spectroscopic signature, discussed in the next section, delayed its detection in the interstellar medium (ISM).

In fact, the original extra-terrestrial detection of H_3^+ was an *in situ* detection on Jupiter by Voyager-2 using mass spectrometry (Hamilton et al. 1980). Coincidentally, this discovery was approximately contemporaneous with the original laboratory measurement of the spectrum of the ion by Oka (1980). The spectrum of H_3^+ was originally observed in Jupiter (Drossart et al. 1989); notably, this observation relied heavily on high-accuracy first-principles predictions of both the frequency and the intensity of the observed lines (Miller & Tennyson 1988c). The spectrum of H_3^+ has been observed in the atmospheres of Uranus (Trafton et al. 1993) and Saturn (Geballe et al. 1993), but not so far of Neptune (Melin et al. 2011).

The long campaign to detect interstellar H_3^+ (Martin et al. 1961, Oka 1981, Geballe & Oka 1989) eventually succeeded when Geballe & Oka (1996) found the signature of H_3^+ in absorption against starlight in giant molecular clouds. McCall et al. (1998) subsequently detected H_3^+ in significant concentration in diffuse clouds using the same technique. Searches for H_3^+ elsewhere in the Universe have proved more controversial with a tentative detection in the remnants of supernova SN1987a (Miller et al. 1992) and a claimed detection in a protoplanetary disk, which could not be verified (Goto et al. 2005). Note that while much observational work has concentrated on H_3^+ , models suggest that all deuterated isotopologues, even D_3^+ , can occur in significant quantities in the ISM (Walmsley et al. 2004).

While H_3^+ is a vigorous proton donor, it is often destroyed via dissociative recombination (DR):



Laboratory measurement of the rate of DR long proved controversial (Larsson 2000, Larsson et al. 2008), but DR is now known from both measurement (McCall et al. 2003, Kreckel et al. 2010) and theory (Kokoouline et al. 2001, Fonseca dos Santos et al. 2007) to be rapid. Studies have also shown that the DR rate is state dependent and that the high symmetry of H_3^+ opens avenues for population trapping in rotationally-excited

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levels (Kreckel et al. 2002, Kreckel et al. 2004, Mizus et al. 2017), an effect which has also been observed in the ISM (Goto et al. 2002).

The dynamical characteristics of the H_3^+ ion have been the subject of a number of reviews (Oka 1992, Miller & Tennyson 1992, McNab 1995, Tennyson 1995, Polyansky et al. 2012, Oka 2013). The first-principles computation of the spectrum, from the microwave to the ultraviolet, of a molecule such as H_3^+ relies on a number of steps (Lodi & Tennyson 2010) which require extending to treat the observed spectrum above dissociation (Carrington & McNab 1989*b*). The accurate prediction of energies and frequencies requires the accurate solution of the electronic structure problem on a grid of points and the analytic representation of these points to give a potential energy surface (PES). An accurate treatment of the nuclear motion problem should then follow. This is facilitated by the fact that use of exact nuclear-motion kinetic energy operators, which has long been a feature of nuclear motion calculations on H_3^+ (Carney et al. 1978), is straightforward. Determination of contributions to the PES (Császár et al. 1998), often neglected in more approximate treatments, due to relativity, quantum electrodynamics (QED), and the breakdown of the Born–Oppenheimer (BO) approximation also need to be computed. For transition intensities this also requires the calculation and representation of accurate dipole moment surfaces (DMS).

More than a decade ago, Mielke et al. (2003) declared, based on a model developed by two of the present authors (Polyansky & Tennyson 1999), that the spectrum of H_3^+ was a solved theoretical problem. This model, which as we show is characterized by a fortuitous cancellation of errors, is discussed further below and provides our starting point for high-accuracy computations of the rovibrational spectra of the H_3^+ system. Before that we provide a brief overview of the unique spectroscopic properties of H_3^+ and its isotopologues. We then briefly consider first-principles computations on isotopologues of diatomic hydrogen (a four-body system), which can indeed be classed as solved problems. We then move to H_3^+ (a five-body system), considering in turn electronic structure computations, nuclear motion treatments, and representation of effects beyond the BO approximation, the latter being particularly important for this system. The accurate computation of transition intensities is then considered before we provide some comments on future directions and developments.

2. Overview of the spectrum of H_3^+

Our experimental knowledge about the rovibronic spectrum of H_3^+ is rather limited. The equilibrium structure of H_3^+ in its ground electronic state has D_{3h} point-group symmetry, due to the $3c - 2e$ bonding present in the ion. As a highly symmetric species, H_3^+ does not possess a permanent dipole moment, the usual prerequisite for pure rotational transitions. It has been suggested theoretically that distortions of the ion as it rotates should lead to an observable spectrum (Pan & Oka 1986, Miller & Tennyson 1988*a*); however, this has yet to be seen. Calculations also suggest that the ion distorts in the presence of a strong magnetic field (Medel Cobaxin &

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Alijah 2013). Similarly, there are no experimentally-known electronically-excited states of H_3^+ , despite considerable theoretical work on the spectroscopy of the metastable first-excited $^3\Sigma_u^+$ state (Schaad & Hicks 1974, Ahlrichs et al. 1977, Wormer & de Groot 1989, Preiskorn et al. 1991, Friedrich et al. 2001, Sanz et al. 2001, Cuervo-Reyes et al. 2002, Cernei et al. 2003, Alijah et al. 2003, Alijah & Varandas 2004, Viegas et al. 2004, Viegas et al. 2005, Varandas et al. 2005, Alijah & Varandas 2006*b*, Alijah & Varandas 2006*a*, Mendes Ferreira et al. 2008, Alijah & Kokkoulina 2015).

This leaves rotation-vibration transitions, which have been observed in the infrared and visible regions, as the only available spectroscopic handle on the ion. Even here it might appear that there are slim pickings, as H_3^+ has two vibrational modes: a symmetric and hence infrared-inactive stretching mode, ν_1 , and a degenerate bending mode, ν_2 . It was the ν_2 mode that Oka (1980) originally detected. However, it transpires that ‘forbidden’ stretching transitions can also be observed (Miller, Tennyson & Sutcliffe 1990, Xu et al. 1992) and the overtones are also strong (Miller & Tennyson 1988*c*, Majewski et al. 1989, Lee et al. 1991, Dinelli et al. 1992, Dinelli et al. 1997). This leads to a rich spectrum of rotation-vibration transitions, whose observation now extends to visible wavelengths (Kreckel et al. 2008, Pavanello, Adamowicz, Alijah, Zobov, Mizus, Polyansky, Tennyson, Szidarovszky, Császár, Berg, Petignani & Wolf 2012). These lines probe states which lie above the barrier to linearity of the molecular ion, which, for H_3^+ , lies at about $10\,000\text{ cm}^{-1}$ (Morong et al. 2009). Linearity is a monodromy point (Child et al. 1999) and above that energy there are a number of added complications in the theoretical treatment and understanding of the spectra; some of these are discussed below.

There are several compilations of H_3^+ experimental spectroscopic data (Kao et al. 1991, Lindsay & McCall 2001, Furtenbacher, Szidarovszky, Mátyus & Császár 2013); the most recent of these was performed by Furtenbacher, Szidarovszky, Mátyus & Császár (2013), who employed the MARVEL (Measured Active Rotation-Vibration Energy Levels) code (Furtenbacher et al. 2007, Furtenbacher & Császár 2012*a*, Császár et al. 2016) to provide a list of empirical energy levels which can be used to benchmark accurate first-principles computations. We note, in particular, that recent experiments (Crabtree et al. 2012, Wu et al. 2013, Hodges et al. 2013, Perry et al. 2015, Jusko et al. 2016, Yu et al. 2017) using frequency combs have provided some particularly high-accuracy transition wavenumbers which can be used to benchmark future, further improved theoretical treatments.

Spectra of deuterated H_3^+ isotopologues have also been studied (Lubic & Amano 1984, Foster et al. 1986, Polyansky & McKellar 1990, Jusko et al. 2016, Yu et al. 2017). Both H_2D^+ and D_2H^+ have permanent dipole moments due to separation between the centre-of-mass and the centre-of-charge; see Jusko et al. (2017) and references therein for a discussion of the observed rotational spectrum. Furtenbacher, Szidarovszky, Fábri & Császár (2013) provide empirical energy levels for these asymmetric-top species. The infrared spectrum of D_3^+ has also been observed (Shy et al. 1980, Amano et al. 1994), although less is known about the spectrum of this species than about those of the other

Table 1. Summary of empirical (MARVEL) energy levels determined for H_3^+ (Furtenbacher, Szidarovszky, Mátyus & Császár 2013) and two of its deuterated isotopologues (Furtenbacher, Szidarovszky, Fábri & Császár 2013), given for different components of the experimental spectroscopic networks (SN) of the ions.

Molecule	SN component	number
H_3^+	<i>ortho</i>	259
	<i>para</i>	393
	floating	105
	sum	757
H_2D^+	<i>ortho</i>	63
	<i>para</i>	46
	floating	14
	sum	123
D_2H^+	<i>ortho</i>	52
	<i>para</i>	52
	floating	27
	sum	131

deuterated isotopologues.

No discussion of the spectroscopy of H_3^+ is complete without consideration of the remarkable and rich near-dissociation spectra of the system discovered by Carrington et al. (1982). This spectrum, which was systematically mapped out over the following years (Carrington & Kennedy 1984, Carrington & McNab 1989*a*, Carrington et al. 1993, Kemp et al. 2000), remains unassigned and still presents a major challenge to theory for a system which only has two electrons. Perhaps some spectroscopic measurements on the near-dissociation spectrum of H_3^+ will be performed in the near future using a well-characterised (cold) source of ions and a multiphoton approach. Such a project could be performed hand-in-hand with theory; it would appear to be the best way to understand the seemingly rich dynamics at and beyond the first dissociation limit.

3. Empirical (MARVEL) rovibrational energy levels

H_3^+ drives the chemistry in many cold parts of the universe, where only barrierless ion-molecule reactions are feasible, and it is also a tracer of the chemistry of the interstellar medium (Miller et al. 2010). Therefore, it is important to know as much and as accurately as possible about the rovibrational energy level structure of this highly stable molecular ion.

Table 1 gives a summary of the MARVEL analyses of the experimental spectroscopic data available for H_3^+ , H_2D^+ , and D_2H^+ . The MARVEL analysis starts with the representation of the observed transitions data by an experimental spectroscopic network

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(SN) (Császár & Furtenbacher 2011, Furtenbacher & Császár 2012b). In the absence of transitions between *ortho* and *para* states, the spectroscopic data of H_3^+ should form two principal components (PC) comprising transitions within the *ortho* and *para* states, respectively. However, in practice the experimental data often define further components not attached to the PCs of the experimental SN by any measured transitions. These components are known as floating components (FC) (Császár & Furtenbacher 2011).

As shown by Furtenbacher, Szidarovszky, Mátyus & Császár (2013), of the 1610 measured transitions for H_3^+ available then, reported in 26 sources, 1410 could be validated, a further 105 transitions belong to FCs, while the rest had to be excluded from the final MARVEL analysis. Despite the difficulties measuring the spectra of an ion without a dipole moment, the spectral range covered by the experiments is wide, between 7 and 16 506 cm^{-1} . This experimental dataset defines 13 vibrational band origins (VBO), with the highest J value of only 12, with a typical uncertainty of about 0.005 cm^{-1} . Since 2013 results from two high-accuracy measurements have been reported (Perry et al. 2015, Jusko et al. 2016). These transitions improve the accuracy of the empirically-determined energy levels but do not alter in any significant way the conclusions detailed here. As of today, the number of validated and thus recommended experimental-quality rovibrational energy levels of H_3^+ is 652, of which 259 belong to *ortho*- H_3^+ ($I = 3/2$) and 393 to *para*- H_3^+ ($I = 1/2$), where the quantum number I refers to the total nuclear spin of the system.

There have been lot fewer experimental studies dealing with the spectra of the deuterated ions. In fact, 13 and 9 sources dealt with H_2D^+ and D_2H^+ , respectively. These measurements define only 7 and 6 VBOs for H_2D^+ and D_2H^+ , respectively. The scarcity of experimental data means that our understanding of the rotational states of the (0 1 0) VBO of H_2D^+ is complete only to $J = 2$, and for all higher-lying VBOs and J values the information is highly incomplete. Two pure rotational transitions of H_2D^+ are important from an astrochemical point of view, the 372.4 GHz ($1_{10} - 1_{11}$) transition (Amano & Hirao 2005) of *ortho*- H_2D^+ and the 1370 GHz ($1_{01} - 0_{00}$) transition (Asvany et al. 2008) of *para*- H_2D^+ . Recently Jusko et al. (2017) measured these and related transitions of D_2H^+ with outstanding accuracy. Yu et al. (2017) reported the measurement of further lines of D_2H^+ with similar accuracy. The extensive variational computations of the rovibrational energy levels of D_2H^+ , performed by Furtenbacher, Szidarovszky, Fábri & Császár (2013) and Alijah & Beuger (1996), are in good agreement with each other. A reliable labeling of most of the computed rovibrational states is provided by Furtenbacher, Szidarovszky, Fábri & Császár (2013), based on a rigid rotor decomposition (RRD) analysis (Mátyus et al. 2010). The few discrepancies between the two studies are discussed by Furtenbacher, Szidarovszky, Fábri & Császár (2013). Note that the work of Furtenbacher, Szidarovszky, Fábri & Császár (2013) attempted to label several measured transitions left unlabeled by Polyansky & McKellar (1990) and Shy (1982); validation of these assignments awaits further experimental studies.

4. Computations on diatomic hydrogen: H_2 and H_2^+

Computation of the rovibrational energy levels of the H_2 and H_2^+ molecules provides precise and accurate information which can be used to understand similar computations on H_3^+ . Although comparison with experimental results gives the ultimate criteria for establishing the accuracy of a theoretical model, it does not easily provide estimates of the accuracy of the components of the model. In particular, the separate comparison of the BO energy and the adiabatic, non-adiabatic, relativistic, and QED energy corrections cannot be executed by a direct comparison of computed H_3^+ spectra with experimental ones. Since the computation of energies and energy corrections can be performed almost exactly for H_2 and H_2^+ , a comparison with the corresponding values of H_3^+ can give valuable insight. First of all, when there is no way to even estimate the order of magnitude of certain corrections for triatomic H_3^+ , data on diatomic H_2 and H_2^+ do give these. Second, the methods of computation of energy corrections for polyatomics often follow the methods developed for the diatomic hydrogen species.

As mentioned by Korobov (2006) (see also references given there), variational determinations of non-relativistic energies for H_2^+ and HD^+ have reached a precision of $10^{-15} - 10^{-30} E_h$ (that is $10^{-10} - 10^{-25} \text{ cm}^{-1}$). This unprecedented precision is due to the simplicity of these three-particle systems. Note that there is a demand for such high-accuracy computations for the purpose of high-accuracy determination of the electron-proton mass ratio using spectroscopic techniques (Ubachs, Bagdonaite, Salumbides, Murphy & Kaper 2016, Ubachs, Koelemeij, Eikema & Salumbides 2016). Improvement of non-relativistic energies by Moss (1993) to 10^{-5} cm^{-1} is already sufficient for the purpose of deriving effective vibrational masses for use within the Bunker & Moss (1980) non-adiabatic model. This model was an important development, as it could be validated using highly accurate experimental H_2^+ data, see Polyansky & Tennyson (1999). Hilico et al. (2000) further improved the accuracy of the energy computations to $10^{-14} E_h$. There is an extensive literature on non-relativistic H_2^+ calculations, but the references given provide a sufficiently detailed picture for our purposes. The accuracy achieved at present for the non-relativistic energy computations of H_2^+ and its deuterated analogs can be considered as providing an ideal benchmark for studies on H_3^+ and its D-analogs.

Extension of the electronic structure treatment to include relativistic and QED theory (Korobov 2006) reduced the discrepancy between calculations and experiment (Koelemeij et al. 2007, Roth et al. 2006) to only about 100 kHz ($\approx 3 \times 10^{-6} \text{ cm}^{-1}$). Korobov (2006) supplemented the relativistic and QED corrections, of the order of α^4 , where α is the fine-structure constant, by corrections up to order α^6 . The resulting uncertainties in the low-lying energies are about 300 MHz for the α^3 and 2 MHz for the α^4 terms.

Inclusion of α^3 and α^4 relativistic and QED corrections in the first-principles determination of energies for H_2 results in a discrepancy between theory and experiment for both the low-lying levels and the dissociation energy, of only about 1 MHz ($\approx 3 \times 10^{-5}$

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cm^{-1}) (Komasa et al. 2011, Pachucki & Komasa 2014, Puchalski et al. 2017). The contribution of QED terms to these energies is given in the Supplementary Material of Komasa et al. (2011) and its magnitude is up to 0.2 cm^{-1} . The latest computations include terms up to α^6 (Puchalski et al. 2016).

As mentioned before, the contribution of non-adiabatic effects in H_2 and H_2^+ can be computed extremely accurately (Fábri et al. 2009). However, most interesting for our purposes is the use of these results for comparing the calculations of non-adiabatic effects using the methods applicable also for polyatomic molecules, in particular H_3^+ .

Bunker & Moss (1980) developed perturbatively a functional form for the non-adiabatic correction. This approximation can be expressed in the form of two different effective nuclear masses, one for vibrations and another one for rotations. These differ from the actual nuclear masses and mimic the non-adiabatic corrections. These masses may have a coordinate dependence, in case of a diatomic molecule the distance between the two nuclei. Moss (1996) simplified this dependence and represented both rotational and vibrational masses as constants. He (a) fixed the rotational mass correction to zero, that is the value of the rotational mass is equal to the nuclear mass, and (b) fitted the vibrational mass so that its use would reproduce the value of his non-relativistic energies, calculated with an accuracy of 10^{-5} cm^{-1} . This model was generalised to H_3^+ by Polyansky & Tennyson (1999) as discussed extensively below. An alternative, empirical approach was suggested by Schiffels et al. (2003a), who introduced energy-dependent corrections to the band origins. This model was extended by Alijah (2010) to higher energies and, as also discussed below, has been tested for the H_3^+ molecule. When higher accuracy is necessary for the representation of non-adiabatic effects, the coordinate dependence of the rotational and vibrational masses should be taken into account (Schwartz & Le Roy 1987, Jaquet & Kutzelnigg 2008). The most recent calculation of non-adiabatic effects with a representation in the form of coordinate dependent rotational and vibrational masses is given by Pachucki & Komasa (2009).

Dickenson et al. (2013) presented measurements and *ab initio* computations of the vibrational fundamentals of H_2 , HD, and D_2 with an accuracy of $2 \times 10^{-4} \text{ cm}^{-1}$, with a similar agreement obtained for the dissociation energy (Ubachs, Koelemeij, Eikema & Salumbides 2016). For these studies the calculations were based on a fully correlated basis of exponential functions (Pachucki & Yerokhin 2013) plus corrections for BO (Pachucki & Komasa 2014), relativistic, and QED effects. At this (high) level of accuracy, theory and experiment are in complete agreement.

There are other approaches to move beyond the usual BO approximation. One approach, the simultaneous consideration of all electronic states, was explored by Schwenke (2001) and Fábri et al. (2009). In particular, Fábri et al. (2009) computed energies for the three-body H_2^+ system using finite, nuclear masses while maintaining the notion of a potential energy curve. Thus far this many coupled-states approach has not yielded high-accuracy results, though it has improved our understanding of non-adiabatic treatments of molecules containing heavier nuclei (Schwenke 2003, Tennyson et al. 2002).

Table 2. Summary of *ab initio* H_3^+ potential energy surfaces with spectroscopic accuracy. The accuracy given is the difference in the lowest energy point to that computed by Pavanello et al. (2009).

Authors	Method	Dipole?	N_{points}	Accuracy/cm ⁻¹	Designation
Meyer et al. (1986)	Full CI	yes	69	160	MBB
Lie & Frye (1992)	Hylleraas-CI	yes	69	9	
Röhse et al. (1994)	CISD-R12	no	69	1	
Cencek et al. (1998)	ECG	no	69	0.04	
Bachorz et al. (2009)	ECG	no	5900	0.04	
Pavanello et al. (2012)	ECG	yes	41655	0.01	GLH3P

An alternative approach is not to make the BO approximation and treat the electron and nuclear motions simultaneously. A fully non-Born–Oppenheimer treatment of H_2 was recently presented by Jones et al. (2017). They produced very accurate results, which gave energy levels systematically 0.02 cm⁻¹ above those presented by Komasa et al. (2011), who employed a more conventional approach which makes an initial BO approximation, as discussed above. Of course, this shift means that the vibrational fundamental of H_2 is still predicted with an accuracy similar to the measurement, but the dissociation energy is slightly underestimated.

5. Electronic structure of H_3^+

There is a long history of electronic structure computations on the two-electron H_3^+ system. At the dawn of quantum chemistry, calculations by Coulson (1935) demonstrated the unexpected stability if the ion and that it has an equilateral triangle equilibrium structure. The first Born–Oppenheimer PES which gave results that approached spectroscopic accuracy was due to Meyer et al. (1986) (MBB); the MBB surface is not entirely *ab initio* in that a single parameter was tuned to improve the frequency of the ν_2 bending fundamental. Calculations using this surface played an important role in assigning H_3^+ spectra, both in the laboratory (Majewski et al. 1989, Lee et al. 1991, Polyansky et al. 1993) and in space (Drossart et al. 1989, Miller, Joseph & Tennyson 1990). MBB used a full configuration interaction (FCI) method with a relatively large basis on a carefully designed grid of 69 points to define their PES. This grid became standard in many subsequent calculations.

Table 2 charts the improvement in high-accuracy PES computations starting with the MBB PES. Subsequent studies all included explicit treatment of the electron-electron coordinate, r_{12} , in the electronic structure calculation. As can be seen this leads to a dramatic improvement in the accuracy of the PES. Anderson (1992) used a Monte Carlo treatment to obtain, within a quoted uncertainty of about 0.2 cm⁻¹, the precise electronic energy for H_3^+ at its equilibrium geometry. In practice this value

Table 3. Summary of less accurate *ab initio* H_3^+ potential energy surfaces

Authors	Method	Dipole?	N_{points}	Accuracy/ cm^{-1}
Aguado et al. (2000)	Full CI	no	8469	20
Barragan et al. (2011)	DFT	no	69	315
Viegas et al. (2007)	Full CI	no	8177	5
Velilla et al. (2008)	Full CI	no	8469	20
This work	Full CI, CBS	yes	2500	0.5

has been superseded by very extensive computations using explicitly correlated Gaussian (ECG) functions. The largest of these computations, due to Pavanello et al. (2009), is used to benchmark the accuracy of the various PES's considered in Table 2.

The model due to Polyansky & Tennyson (1999) used the PES developed by Cencek et al. (1998), augmented by their relativistic correction and an improved fit (Polyansky et al. 1995) to their adiabatic corrections. To allow for non-adiabatic effects, Polyansky & Tennyson (1999) adapted the approach of Bunker & Moss (1980), who advocated the use of separate, constant masses for the vibrational and rotational motions. Polyansky & Tennyson (1999) used the nuclear mass for the rotational motion and effective vibrational masses based on the ones recommended for the H_2^+ isotopologues by Moss (1996). It should be noted that the Tennyson & Sutcliffe (1982) Hamiltonian used by Polyansky & Tennyson (PT) is formulated to exploit the cancellation between a vibrational and a rotational term. Use of distinct masses for these two motions therefore results in an extra, non-Born–Oppenheimer, term in the Tennyson–Sutcliffe Hamiltonian.

The PT computations reproduced the low-lying rotation-vibration energy levels of H_3^+ , H_2D^+ , D_2H^+ , and D_3^+ to within a few hundredths of a cm^{-1} . Nevertheless, the accuracy remains worse than that of computations based on the use of the best semi-empirical spectroscopically determined PES (Dinelli et al. 1995), which contained explicit allowance for adiabatic but not for non-adiabatic effects. Furthermore, PT only considered low-lying rotational states as their model makes no allowance for non-adiabatic effects in the rotational motion, which should grow rapidly, as J^4 , with rotational excitation, where J is the quantum number characterising the overall rotation. In what follows the model of PT is used as a baseline against which more recent studies are compared.

For completeness, in Table 3 we also present a list of less accurate electronic structure calculations of H_3^+ PESs based on the use of more conventional electronic structure methods, including density functional theory (DFT). The reason for considering these calculations is twofold. First, these less accurate methods make it inexpensive to compute many more points than the more accurate ones, which resulted

in purely *ab initio* PESs, when more accurate methods were still too expensive to be used to provide the coverage needed for global calculations, see Polyansky et al. (2000) for an example. These calculations can potentially provide an “unlimited” number of points for studies of global PESs if needed. Second, such calculations provide the benchmark of the methods used when applied to systems with more electrons, such as H_5^+ (Xie et al. 2005, Aguado et al. 2010), for which the more sophisticated methods listed in Table 2 cannot be used.

To help understand the BO PES of H_3^+ , for this study we computed 2500 full configuration interaction (FCI) energy points, using the standard electronic structure code MOLPRO (Werner et al. 2012), with aug-cc-pVnZ ($n = 5$ and 6) basis sets and produced a complete basis set (CBS) FCI surface, which differs from the ECG PES in absolute energy by less than 1 cm^{-1} . Nuclear motion calculations using this PES reproduce the MARVEL energy levels of H_3^+ with a standard deviation of 0.5 cm^{-1} , which is only 5 times worse than with the most accurate PES currently available.

6. Beyond the non-relativistic treatment

Polyansky & Tennyson employed the relativistic correction surface computed by Cencek et al. (1998). This correction is about 3 cm^{-1} but varies only weakly with internuclear separation, meaning that its contribution to any calculated transition frequency is relatively minor. Bachorz et al. (2009) subsequently extended this surface, which they computed as the expectation value of the complete Breit–Pauli relativistic Hamiltonian using very accurate wave functions based on ECGs. This relativistic surface, as far as we are aware, meets the requirements for a high-accuracy calculation.

As noted by Lodi et al. (2014), the smallness and smoothness of the relativistic correction in H_3^+ is caused by the almost complete cancellation between the two most important first-order corrections, the one-electron mass-velocity and Darwin terms, together usually denoted as MVD1 (Tarczay et al. 2001). This cancellation of contributions results in another interesting effect. Superficially the QED contribution to the energy levels should be much less than the relativistic contribution, as QED effects are generally about 5 % of the relativistic effect. However, as QED is 5 % of only one part of the scalar relativistic effect – that is of the one-electron Darwin term (Pyykkö et al. 2001), in the case of H_3^+ the overall contribution of QED to the energy levels is comparable to the overall relativistic (MVD1) one. This means that it is necessary to allow for the QED effects in all accurate calculations of the H_3^+ spectrum.

The relativistic surfaces used by Pavanello, Adamowicz, Alijah, Zobov, Mizus, Polyansky, Tennyson, Szidarovszky & Császár (2012) and Polyansky et al. (2012) were limited to $30\,000 \text{ cm}^{-1}$, as all experimental energy levels with which comparisons could be made lie well below this energy threshold. For the purpose of making the ECG-based global H_3^+ potential (named GLH3P by Pavanello, Adamowicz, Alijah, Zobov, Mizus, Polyansky, Tennyson, Szidarovszky & Császár (2012)) a fully global potential, a fit of the relativistic energies to a global set of geometries is mandatory. We produced such a

fit as part of this study and the resulting analytic surface reproduces the set of *ab initio* points with a standard deviation of about 0.02 cm^{-1} . Geometries with energies from 0 to $43\,000\text{ cm}^{-1}$ are used in the fit and the resulting global relativistic surface contains 40 constants. This surface is given in the Supplementary Material. An outstanding issue is the stability of this and other surfaces over the entire range of coordinates. A high accuracy surface that satisfies this criterion which is essential for studies of spectra above dissociation as well as reaction dynamics is currently under construction.

Consideration of the effects introduced by QED can be important for the accurate prediction of vibration-rotation spectra of even H-containing molecules. Lodi *et al.* (2014) used the methodology of Pyykkö *et al.* (2001) to compute QED corrections to the spectrum of H_3^+ . Lodi *et al.* found that including QED effects leads to shifts of about 0.1 cm^{-1} in the predicted vibrational band origins but combining them with the Polyansky & Tennyson model actually made the results worse by roughly this amount. This was the first indication that the excellent results of PT may have been, at least partially, fortuitous.

7. Fitting the potential energy surface

There are a number of global surfaces available for the ground electronic state of the H_3^+ ion (Miller & Tennyson 1987, Miller & Tennyson 1988*c*, Prosmiti *et al.* 1997, Polyansky *et al.* 2000, Aguado *et al.* 2000, Viegas *et al.* 2007, Velilla *et al.* 2008, Pavanello, Adamowicz, Alijah, Zobov, Mizus, Polyansky, Tennyson, Szidarovszky & Császár 2012). As can be seen from Table 2, a number of high-accuracy PESs were based on the 69 point grid originally designed by Meyer *et al.* (1986). Clearly, when constructing global surfaces from *ab initio* data a much more extensive grid is required.

Pavanello, Adamowicz, Alijah, Zobov, Mizus, Polyansky, Tennyson, Szidarovszky & Császár (2012) computed a high-accuracy PES with over 40 000 points; this allowed them to both produce a global surface and test the coverage of MBB's 69-point grid. Polyansky *et al.* (2012) compared the multipoint GLH3P fit of Pavanello, Adamowicz, Alijah, Zobov, Mizus, Polyansky, Tennyson, Szidarovszky & Császár (2012) with a fit to just the standard 69 points. This gave an interesting result: while differences for some of the vibrational levels were found to be very small, there are differences of a few tenths of a cm^{-1} for levels up to the barrier to linearity and between a few to tens of cm^{-1} for the levels above it. This demonstrates that MBB's 69 points are insufficient to accurately characterise the PES of H_3^+ .

In order to understand better the influence of the number of points and the density of the grid on the final PES, we computed several PESs using 69 MBB points, then the same 69 points plus 300 points and so forth up to the full GLH3P grid. These calculations, summarised in Table 4, show that the use of additional points in the PES fit has a significant effect on the computed vibrational energies. In particular, moving from 69 points to a much larger set gradually *increases* the observed minus calculated residues for vibrational term values lying below 7000 cm^{-1} from about 0.05 cm^{-1} to

Table 4. Comparison of calculated vibrational term values for several different PESs. Computed energies, in cm^{-1} , are given as observed minus calculated, and they are compared to the empirical MARVEL energies of Furtenbacher, Szidarovszky, Mátyus & Császár (2013). All calculations used relativistic, QED and DBOC corrections plus the PT non-adiabatic model.

$v_1v_2\ell$	MARVEL	GLH3P	BO-69	BO-2500	BO-69	BO-369
	Expt.	ECG	Full CI	Full CI	ECG	ECG
0 1 1	2521.408	0.11	0.17	0.11	0.08	0.12
0 2 2	4998.048	0.15	0.16	0.12	0.08	0.16
1 1 1	5554.061	-0.14	0.19	-0.14	-0.03	-0.09
0 3 3	7492.911	0.13	-0.03	-0.03	-0.07	0.13
2 2 2	10645.377	0.06	1.51	-0.76	3.14	0.06
0 5 1	10862.901	0.15	1.95	-1.00	1.33	0.20
3 1 1	11323.096	-0.03	1.42	-1.46	3.05	0.01
0 5 5	11658.397	0.08	1.45	-1.39	3.47	0.08
2 3 1	12303.363	0.02	0.78	-2.03	2.77	-0.06
0 6 2	12477.378	-0.02	1.18	-2.41	2.07	-0.04
0 7 1	13702.372	-0.22	1.65	-5.21	2.05	-0.26
0 8 2	15122.801	0.15	2.39	-5.59	7.35	0.00

about 0.1 cm^{-1} . However, levels above 7000 cm^{-1} are improved in comparison with calculations using the Polyansky & Tennyson (1999) surface, and result finally in the accuracy of GLH3P, demonstrated by Pavanello, Adamowicz, Alijah, Zobov, Mizus, Polyansky, Tennyson, Szidarovszky & Császár (2012) and Polyansky et al. (2012) to be about 0.1 cm^{-1} up to $17\,000 \text{ cm}^{-1}$. These calculations demonstrate that the extremely high accuracy of the Polyansky & Tennyson (1999) calculations for the then available levels, which all lie below 7000 cm^{-1} , was indeed fortuitous.

8. Nuclear motion computations

Accurate solutions of the nuclear motion problem for low-lying states of H_3^+ and its isotopologues have been obtained by a number of groups (Neale et al. 1996, Polyansky & Tennyson 1999, Alijah, Hinze & Wolniewicz 1995, Alijah, Wolniewicz & Hinze 1995, Alijah & Beuger 1996, Jaquet 2002, Schiffels et al. 2003a, Schiffels et al. 2003b, Velilla et al. 2008, Bachorz et al. 2009, Alijah 2010, Jaquet 2010, Furtenbacher, Szidarovszky, Fábri & Császár 2013, Mátyus et al. 2014, Pavanello, Adamowicz, Alijah, Zobov, Mizus, Polyansky, Tennyson, Szidarovszky, Császár, Berg, Petrignani & Wolf 2012). These extensive studies confirm that within the BO approximation different approaches to the variational solution of the nuclear motion problem all yield essentially the same answers and that the numerical uncertainties introduced at this stage of the calculation are negligible. This means that for studying spectra of H_3^+ the principal issue for the

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accurate determination of rovibrational states is the method used to treat the breakdown of the BO approximation. This aspect of H_3^+ spectroscopy is considered in detail in section 9.

The (nearly) complete set of bound vibrational levels of H_3^+ and its deuterated isotopologues have also been determined several times using accurate PESs (Munro et al. 2005, Munro et al. 2006, Barletta et al. 2006, Tennyson et al. 2006, Szidarovszky et al. 2010). Such studies require a PES which has correct dissociative behavior, a property which few fitted PESs possess. The so-called PPKT2 PES (Polyansky et al. 2000, Munro et al. 2006) satisfies this criterion. A few related relevant results are as follows: (a) the lowest dissociation energy (D_0) of H_3^+ , corresponding to the reaction $H_3^+ \rightarrow H_2 + H^+$, is $34\,912\text{ cm}^{-1}$ (Munro et al. 2006); (b) below D_0 there are at least 688 even-parity and 599 odd-parity vibrational states, as computed by Szidarovszky et al. (2010). Computing the last few states below the first dissociation limit is rather problematic for all molecules. This is partly due to the fact that rovibrational Hamiltonians expressed in internal coordinates must have singular terms in their kinetic energy part, requiring a careful choice of basis functions in variational and near-variational treatments. Furthermore, the last few states extend to very large values along the dissociation coordinate, requiring the use of extended basis sets (Munro et al. 2005). The long-range nature of the H_3^+ potential results in the system supporting a number of asymptotic vibrational states (Munro et al. 2005). Trial numerical studies suggested that these states are not that sensitive to the precise form of the long-range potential used (Tennyson et al. 2006). However, there is definitely more work to be done on this problem.

9. Born–Oppenheimer breakdown

The mass-dependent non-BO effects can be separated into adiabatic, or diagonal Born–Oppenheimer correction (DBOC) (Handy et al. 1986, Kutzelnigg 1997), and non-adiabatic effects.

The first adiabatic surface was determined by Tennyson & Polyansky (1994) by inverting experimental data. More recently *ab initio* techniques have been used for the same purpose. In particular, the adiabatic surface used by Pavanello, Adamowicz, Alijah, Zobov, Mizus, Polyansky, Tennyson, Szidarovszky & Császár (2012) and Polyansky et al. (2012) for their GLH3P calculations was produced (as in the case of the relativistic surface) up to $30\,000\text{ cm}^{-1}$, as all the experimentally known energy levels were much below this value. The surface was obtained by the fitting of 3300 *ab initio* points with a standard deviation of 0.017 cm^{-1} employing 98 parameters. In order to make the GLH3P surface genuinely global, we fitted 5500 points (out of 6000 available) for geometries with energies from 0 to $39\,000\text{ cm}^{-1}$. The number of parameters of the surface is 90 and the standard deviation of the fit is 0.22 cm^{-1} . This fit is an order of magnitude worse than that of the above mentioned more limited surface. However, the accuracy is comparable to the accuracy of the BO surface and provides a good basis for

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global nuclear motion calculations. This surface is given in the Supplementary Material, as is a spreadsheet illustrating the effect of correctly treating the adiabatic correction at high energies.

Next, let us consider the non-adiabatic effects on the nuclear motions of H_3^+ . Non-adiabatic effects constitute the weak point of all nuclear motion calculations on H_3^+ . As a result the remaining 0.1 cm^{-1} residues in the computed H_3^+ ro-vibrational energy levels are mainly due the solution of the non-adiabatic problem.

Alijah & Hinze (2006) provided a thorough analysis of the non-adiabatic effect for the rovibrational levels of H_3^+ based on some simple linear and quadratic correction functions. This study was hindered by the fact that basically no accurate experimental rovibrational energies higher than about $10\,000 \text{ cm}^{-1}$ were available in 2006. After the availability of experimental (MARVEL) energy levels, Mátyus et al. (2014) compared the ultimate Born–Oppenheimer rovibrational energies computed utilizing the adiabatic GLH3P PES with the highly accurate MARVEL levels. The exceptional quality of the GLH3P adiabatic PES, namely that it reproduces all the known term values when employing nuclear masses for both rotational and vibrational motion with an RMS error of just 0.19 cm^{-1} , is clear from this comparison.

The model based on constant but motion-dependent masses (different vibrational and rotational masses) provides an appealing choice to represent non-adiabatic effects, as it (a) is conceptually simple; (b) keeps the notion of a PES almost intact (see below); and (c) has been proved to improve computed energies with respect to experimental values, in the case of H_3^+ by a factor of two (Mátyus et al. 2014). The theoretical basis for such a model has been devised for diatomics by Herman & Asgharian (1968) and by Bunker & Moss (1977), who derived effective Hamiltonians incorporating, in the absence of avoided crossings, most of the non-adiabatic effects. Their treatment yielded separate, coordinate-dependent masses for vibration and rotation, and a correction term to the potential, which demonstrates that the effect of non-adiabatic coupling cannot be described solely by adjusting the PES. Introducing different vibrational and rotational masses, but keeping them constant, may be seen as a lowest-order approximation.

The next step would be the introduction of coordinate-dependent mass surfaces (CDMS) for both the rotational and vibrational masses. Mátyus et al. (2014) considered the form of the Hamiltonian when the masses are allowed to have coordinate dependence. They showed that, at least within the fully numerical and black-box-like GENIUSH code (Mátyus et al. 2009, Fabri et al. 2011), both the motion-dependent and the CDMS models can be implemented with relative ease. This opens the route toward a systematic improvement of the theoretical description of second-order non-adiabatic effects in polyatomic molecular systems. Another principal and far-reaching conclusion of this study is that even in the case of constant but motion-dependent masses the computed rovibrational energy levels depend on the embedding of the body-fixed frame utilized for the computation. Among the embeddings tested it was only the Eckart (1935) embedding with a symmetric triangular reference structure which remained invariant under the permutation of the protons. Except for this case of a permutationally invariant

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embedding, an artificial splitting characterizes the computed degenerate rovibrational eigenvalues. This splitting increases with J and exceeds the assumed accuracy of the computation by about $J = 5$.

When optimizing the vibrational mass using 15 selected measured high-accuracy low-energy transitions, see Table I of Mátyus et al. (2014), while keeping the rotational mass constant at the nuclear mass of H, the optimal vibrational mass of the proton turned out to be higher by about one-third of an electron mass than the nuclear mass. This value is substantially less than the optimal mass given by Moss (1996) for H_2^+ as used in the PT model, where the correction is almost half of the mass of an electron. This result is extremely similar to the conclusion of a recent work of Diniz et al. (2013), who obtained a core-mass surface from a simple Mulliken population analysis carried out for H_3^+ . Using this mass surface the authors determined effective masses for each vibrational state in an iterative procedure, and they obtained extremely similar mass corrections for the 00^0 and 01^1 states. Using the optimized vibrational mass of Mátyus et al. (2014), the RMS deviation between the “non-adiabatic” first-principles and the 15 empirical (MARVEL) rovibrational energies becomes only 0.008 cm^{-1} . This is down from an RMS discrepancy of 0.19 and 0.10 cm^{-1} employing the nuclear and the Moss masses, respectively. The improved differences basically correspond to the internal accuracy of the experimental MARVEL energy levels of H_3^+ .

An *ab initio* study by Alijah et al. (2015) of the non-adiabatic coupling terms showed that up to four electronic states need to be included in conventional non-adiabatic dynamical calculations, depending on the accessible nuclear configurations and energy. This demonstrates that the use of motion-dependent masses is the most promising way for further improvement of the computed bound energy levels.

When discussing high accuracy, first principles treatments of H_2^+ and H_2 we noted that computations performed without making the BO approximation gave results competitive with the one based on more conventional treatments augmented by BO breakdown corrections. This is not true for H_3^+ , as it is currently not possible to perform accurate fully non-BO treatments of triatomic species (L. Adamowicz, private communication, 2013; E. Mátyus, private communication, 2016), even though such treatments are possible on five-particle systems with only two heavy particles (atoms) (Stanke et al. 2009).

To conclude this section, let us note that the D_3^+ ion is much less well studied experimentally than H_3^+ . Nevertheless, as the non-adiabatic effects are mass-dependent, the influence of them on the energy levels of D_3^+ is significantly smaller. While there is more information on the levels of H_2D^+ and D_2H^+ , the lower-symmetry of these mixed isotopologues introduces extra, symmetry-breaking non-BO terms (Dinelli et al. 1995) making such a comparison much less straightforward. With an extensive set of D_3^+ experimental energy levels, we could more reliably demonstrate that the remaining 0.1 cm^{-1} residues in H_3^+ energy level calculations are due to non-adiabatic effects and, in other words, that all other components of the calculations are accurate to 0.01 cm^{-1} or better. This would put *ab initio* calculations on the H_3^+ molecular ion in their expected

position between H_2 , with an accuracy of 10^{-4} cm^{-1} , and water (Polyansky et al. 2013) and H_2F^+ (Kyuberis et al. 2015), with an accuracy of 0.1 cm^{-1} for *ab initio* calculations.

10. Transition intensities

Use of H_3^+ spectra for remote sensing, for example during astrophysical applications, relies on transition intensities which in turn establish column densities. However, laboratory experiments rarely prepare H_3^+ ions in thermal equilibrium; a modern exception to this is the cold populations prepared using an ion-trap apparatus (Asvany et al. 2007). This means that absolute laboratory measurements of transition intensities are unusual. Indeed, McKellar & Watson (1998) provided a rare example of an H_3^+ spectrum with absolute intensities; there are a number of other examples where transitions from the same lower state have been measured under the experimental conditions to give accurate relative intensities (Farnik et al. 2002, Asvany et al. 2007, Petrignani et al. 2014).

In the absence of measured line intensities, theory has taken on the role of providing line intensities to aid modeling and remote sensing of H_3^+ ions. These are largely provided in the form of line lists based on either computed transition frequencies (Neale & Tennyson 1995, Sochi & Tennyson 2010) or empirical ones where available (Kao et al. 1991, Mizus et al. 2017). Experience for a number of molecules suggests that accurate intensities are best computed using *ab initio* dipole moment surfaces (DMS) (Lynas-Gray et al. 1995, Tennyson 2014). Computing transition intensities therefore requires accurate wave functions and a high quality *ab initio* DMS. As shown in Table 2, there are a number of DMSs available although not all high accuracy PES computations have been extended to provide a DMS.

Although the non-BO contribution to the transition intensity can be expected to be small (Hobson et al. 2009), the DMS for the asymmetric isotopologues H_2D^+ and D_2H^+ is significantly different from that for H_3^+ . This is a result of the separation of the centre-of-charge and centre-of-mass in the asymmetric systems which leads to a permanent dipole moments of approximately 0.60 D and 0.46 D for H_2D^+ and D_2H^+ , respectively. Again there are no direct measurements of these dipoles or any associated transition intensities.

In the absence of high accuracy, absolute experimental intensity data it is difficult to be definitive about the accuracy of the available DMSs and the associated transition intensities. The most stringent test is currently provided by the relative intensity measurements of Petrignani et al. (2014), who probed 18 lines starting from states with $J = 0$ and 1 at visible wavelengths. These results show that even the relatively simple DMS of Lie & Frye (1992) gives very good results. This DMS is based on calculations performed at the 69 grid points of MBB and a modest fit employing only 7 constants. The much more extensive grid of dipole moments presented by Petrignani et al. (2014) should allow a more extended and possibly more accurate DMS to be produced. Use of this extended grid of points raises issues with fitting similar to those encountered with

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PES fits and discussed above.

11. Behaviour at dissociation

While it is straightforward to compute rovibrational states of H_3^+ and its deuterated isotopologues lying below about $20\,000\text{ cm}^{-1}$, or halfway to dissociation, this is not so for high-lying states. Studies have probed the highest bound rotational states of the H_3^+ system (Miller & Tennyson 1988*b*, Jaquet & Carrington 2013, Jaquet 2013) predicting that the highest bound state has $J = 46$.

In order to study the near dissociation spectrum of H_3^+ observed by Carrington and co-workers, it is necessary to consider vibrationally excited states both just below and just above dissociation. As discussed above, a series of studies have been performed focused on representing all the vibrational states up to dissociation (Henderson & Tennyson 1990, Henderson et al. 1993, Munro et al. 2006, Szidarovszky et al. 2010). Of course it was above dissociation that Carrington and co-workers observed their very complex and structured spectrum. Fully quantal studies approaching the accuracy of experiments in this region are extremely challenging. Mandelshtam & Taylor (1997) performed very early calculations identifying vibrational (Feshbach) resonances. However, at that stage there were no realistic global PESs available. More recent studies identifying resonances (Silva et al. 2008) have been based on more realistic surfaces and have begun to consider the role of rotational motion which gives the shape resonances that are the key to understanding the near-dissociation spectrum (Llorente & Pollak 1988, Chambers & Child 1988). There is clearly a need to do more theoretical work on this problem. As is clear from reviewing the available models, methods, and codes, these future studies would need to combine a highly accurate global PES, including even QED correction, and a good representation of first- and second-order adiabatic corrections, perhaps in the form of coordinate-dependent mass surfaces. Work in this direction is currently being undertaken (Mizus et al. 2018). Furthermore, efficient computation and identification of rovibrational resonance states, including the reliable computation of their intensities, is needed, an area under constant development (Mussa & Tennyson 2000, Zobov et al. 2011, Moiseyev 2011, Szidarovszky & Csaszar 2013).

12. Conclusions

H_3^+ is an astronomically important molecular ion which also provides a key benchmark of theoretical treatments for polyatomic molecules. *Ab initio* treatments of H_3^+ remain many orders of magnitude less accurate than those available for diatomic hydrogenic systems (H_2^+ and H_2). The main unresolved problem for high accuracy predictions of the rotation-vibration spectrum of H_3^+ and its isotopologues is the treatment of non-adiabatic effects beyond the Born–Oppenheimer approximation. A number of methods of including non-adiabatic effects have been explored; the most promising appears to be the use of coordinate-dependent effective masses.

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While vibration-rotation spectra involving low-lying states of H_3^+ is well understood, the same cannot be said of its near-dissociation spectrum. Experimental photodissociation spectra of H_3^+ and its isotopologues recorded three decades ago provide a window into the very complex structure of the nuclear motion states both just below and just above the lowest dissociation limit. This problem still awaits a proper theoretical elucidation.

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